# CEMENT AND LIME MANUFACTURE

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PUBLISHED BY
CONCRETE PUBLICATIONS LIMITED
14 DARTMOUTH STREET, LONDON S.W.1

TELEPHONE: WHITEHALL 4581
TELEGRAPHIC ADDRESS:
CONCRETIUS PARL, LONDON

PUBLISHERS OF
"CONCRETE & CONSTRUCTIONAL ENGINEERING"
"CONCRETE BUILDING & CONCRETE PRODUCTS"
"CEMENT & LIME MANUFACTURE"
"THE CONCRETE YEAR BOOK"
"CONCRETE SERIES" BOOKS, ETC.

VOLUME XI. NUMBER 12 DECEMBER 1938


## Silica Bricks in Vertical Lime Kilns.

By CALCITE.

WHILE the horizontal rotary kiln appears to be gaining favour for lime production, the vertical kiln still has its disciples and enjoys a fair amount of popularity.

A survey of the types of refractories at present used in the vertical kiln would appear to present a mass of contradictions. In the first place, there are ordinary firebricks with alumina contents ranging from perhaps 32 per cent. to 42 per cent., followed by higher grades of aluminous bricks with $Al_2O_3$ contents in the region of 50 per cent. to 60 per cent. (and sometimes higher). In direct contrast to the high-alumina brick comes a siliceous refractory, containing up to 80 per cent. of $SiO_2$, and this type of brick is apparently equally as successful as the aluminous materials. Further, the use of more expensive super-refractories of a basic character, such as a chrome-magnesite brick, is now being advocated. Finally, there is the " straight " silica brick to complete the group, and the remarks which follow apply to this type of brick for use in the vertical kiln.

Fundamentally the technology underlying the production of quicklime is comparatively simple ; briefly it is as follows. Quicklime (CaO) is ordinarily obtained by heating calcium carbonate. The action is reversible

$$CaCO_3 \rightleftharpoons CaO + CO_2,$$

and does not proceed to completion unless facilities are provided for the carbon dioxide to escape. The part the carbon dioxide plays in the reaction is apparent from a consideration of the phase rule. At about 900 deg. C. calcium carbonate is in equilibrium with approximately 760 mm. of $CO_2$ ; hence above 900 deg. C., when the partial pressure of the $CO_2$ exceeds that of the atmosphere, the equation will proceed in a right-hand direction and calcium carbonate will decompose completely unless confined under pressure. In practice a temperature in the neighbourhood of 1,000 deg. C. to 1,100 deg. C. is employed in the vertical

continuous kiln, thus ensuring ready liberation of the $CO_2$ which escapes from the top of the kiln. Limestone is fed in at the top and lime raked out at the bottom.

The absence of any involved chemical reactions limits discussion on kiln refractories more or less to physical or mechanical considerations. The refractory lining is subject to marked erosion and corrosion from the limestone, particularly in the burning zone where scouring action is very severe. The bricks used are thus required to be as dense as possible and of high mechanical strength. These characteristics may be produced fairly easily in a silica brick; grading of the brick-batch and high moulding pressures are necessary to produce a finished product of low porosity and dense structure, while by increasing the lime content of the brick its strength and toughness may be appreciably increased. A normal lime-bonded silica brick, say, for steel-melting or coke-oven purposes, usually has a lime content of 1.5 per cent. to 2 per cent., but a more durable brick for lime kilns is produced if the percentage of lime is increased to 2.5 per cent. and even as high as 3 per cent. One point to observe, however, is that with increase in lime the refractoriness of the brick is lowered; the 2.5 per cent. to 3 per cent. lime-bonded bricks may have a refractoriness from 100 deg. C. to 150 deg. C. lower than those of normal lime content, but the refractoriness of the brick is comparatively unimportant in view of the relatively low temperature in the kiln.

With lower porosity (often as low as 16 per cent. to 18 per cent. in bricks made nowadays) and denseness is coupled almost automatically permeability. A well-finished silica brick invariably has a skin on all its surfaces, and if this is not damaged during the installation the brick has every chance of offering the highest possible resistance to damage by carbon dioxide and other gases present if the kiln is gas-fired. It is true that the original face of the brick will soon be worn away by erosion and corrosion, but nevertheless the skin gives some resistance to permeability at the outset. Once the face of the brick is broken, permeability has to be resisted by the particles of the brick themselves, and this resistance will reach a maximum if the grains are tightly packed and voids reduced to a minimum.

One of the chief failings of silica as a refractory is its inclination to spall, or its inability to withstand temperature variations. In the continuous vertical kiln, however, the question of spalling should not be troublesome, particularly if high-lime-bonded silica bricks are used, for increase in lime content improves the spalling resistance of the brick apart from the added strength imparted to it as already mentioned.

One possible disadvantage to the use of a silica brick compared with, say, firebrick, is the former's higher thermal conductivity. This means that the heat losses from the kiln are higher, which is undesirable. Assuming that the face temperature of the silica brick is about 1,100 deg. C. and the thickness of the lining is 12in., then the temperature of the outer face of the brick will be about 300 deg. C. but this can be improved by insulation. A more efficient

and satisfactory lining is one composed of 9in. of silica brick backed by 3in. of diatomaceous insulating brick instead of merely the 12in. of silica, for then the temperature of the outer face is considerably less at, say, 140 deg. C., while the heat losses in the insulated lining are more than halved compared with the losses from the lining in silica brick only. The high thermal conductivity of silica can thus be counteracted by insulation. In Germany silica bricks appear to be fairly popular for use in vertical lime kilns, but this is hardly the case in this country at the present time. Perhaps the near future will see developments in this direction.

## Effect of Alkalis on Portland Cement Clinker.

THE following note is from the Technical News Bulletin of the United States National Bureau of Standards for September, 1938.

Although the alkalis generally are referred to as being among the minor constituents of Portland cement clinker, it is recognised that $K_2O$ and $Na_2O$ may combine with other oxides present in such a manner as to be of great effect in determining the ultimate composition.

As part of the research programme of the Portland Cement Association Fellowship at the Bureau, the manner in which $K_2O$ is combined in Portland cement clinker is to be established by a series of phase equilibria studies involving $K_2O$ and the other constituents. The results of a previous investigation of the system $CaO$-$K_2O$-$Al_2O_3$ show that $K_2O.Al_2O_3$ is the only compound of $K_2O$ in that system which exists in compositions related to Portland cement compositions. A paper by W. C. Taylor, in the September " Journal of Research," shows that $K_2O.Al_2O_3$ likewise is stable in the presence of $4CaO.Al_2O_3.Fe_2O_3$. Furthermore, the compound $K_2O.Al_2O_3$ can exist in the presence of $2CaO.Fe_2O_3$, which may be present in rare instances in cements having an $Al_2O_3.Fe_2O_3$ ratio less than 0.64.

Phase equilibria studies on mixtures of $K_2O.Al_2O_3$ and the other constituents of cement clinker necessarily must follow. In the event that such studies indicate that $K_2O.Al_2O_3$ is stable in the presence of $3CaO.SiO_2$ and $2CaO.SiO_2$, then it may be that $K_2O.Al_2O_3$ exists in clinker. On the other hand, if $K_2O.Al_2O_3$ reacts with any of these compounds to form a new combination, such as $xCaO.yK_2O.zSiO_2$, then it will be necessary to study the relations of that combination with the various cement constituents $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, etc.

In view of recent discoveries, the latter condition appears to be likely. With the development of the technique for examining polished sections of clinkers in reflected light, a dark prismatic interstitial material has been observed in many commercial cement clinkers. It was found that this material did not occur in alkali-free laboratory preparations, but did exist if either or both $Na_2O$ and $K_2O$ were present. The mean refractive index of this weakly-birefracting phase was found to be near 1.72. No crystals possessing optical properties similar to those of $K_2O.Al_2O_3$ were observed.

# Primary Crushing.

## COMPARISON OF DIFFERENT TYPES.

THE following notes and data are drawn from or based upon three reports (Nos. 1, 2 and 3) issued by the United States Department of the Interior and entitled "Bureau of Mines Report of Investigations 3377." These reports summarise the results of tests carried out on three different commercial crushing plants dealing with stone of large size as quarried from three different quarries.

The performance of five crushers is dealt with, and a brief summary of the principal features of these machines and their duty is given in the following table.

| Type | Feed opening (in.) | Motor H.P. | Feed batches (tons) | Tons per hour |
|---|---|---|---|---|
| (a) Gyratory .. | 36 (curved) | 150 | 5 | 900 |
| (b) Single roll .. | 60 by 36 | 150 | 5 | Varying |
| (c) Jaw .. | 60 by 48 | 200 | 6 | 316 |
| (d) Gyratory .. | 27 (curved) | 200 | 6 | 150 to 900 |
| (e) Jaw.. .. | 48 by 36 | 125 | 4½ | 180 |

The figures for output are based generally upon short-period batches; if the feed were made up of "smalls" or "fines" the rate would be higher, while if the feed were made up of large pieces the rate would be much lower. Large pieces in the single-roll crusher limited the rate considerably owing to the condition of "bite" being deferred; in the meantime the large pieces were reduced by chipping.

The discharge opening of the whole group of crushers varied between 8·4 in. and 4·25 in.; the mean was 5·9 in. No attempt was made to produce stone below the size of opening given. A considerable quantity of small stone, however, was produced in the ordinary procedure of crushing; this cannot be avoided. In crusher (a) with a feed between 34 in. and 24 in., and a mean crusher opening of 4·9 in., no less than 40 per cent. of the product passed through a 3-in. mesh screen and 5 per cent. through a 1½-in. screen.

The general condition of the working faces of the various crushers was as follows:

(*a*) The faces were deeply corrugated except in the lower part where the ridges had worn off.

(*b*) The concave face was quite smooth; the roll had intermittent projecting teeth up to 2 in. deep.

(*c*) Both jaw plates were new, having corrugations of 5 in. pitch and up to 2 in. deep.

(*d*) The mantle and concave face were both corrugated; both were in fair condition.

(*e*) All the jaw plates originally had corrugations of 4 in. pitch and 2 in. deep but had been in service for thirteen years and the depth of the corrugations at the bottom was reduced to possibly ¾ in.

The gyratory crusher (a) and the single-roll crusher (b) operated with the equivalent of a free or non-choke feed. Jaw crusher (c) and gyratory crusher (d) operated with choke feed although no choking appeared to occur; in any case the under-size stone passed through the jaw machines very quickly and thus possibly prevented a choked condition. Choking appears to have occurred in the run-of-quarry feed with jaw crusher (e).

The stone experimented upon was limestone of widely different characteristics (obtained from different quarries) and granite. All stone was quarried by blasting, and the arrangement of the blast holes was such that a good aggregate with the minimum of fines was obtained; block holing was kept to the lowest reasonable figure. The blasted stone was all handled by power shovels having buckets of 2 or 2½ cub. yd. capacity. The stone was conveyed to the crushing plant in skips of 6-ton, 5-ton, and 4½-ton capacity and dumped into the crusher mouth, hopper, or equivalent receptacle in batches of this weight.

The crusher feed was normally comprised of run-of-quarry stone having a maximum dimension of 34 in. or 24 in. (according to the crusher) down to fines. For the purpose of test some batches of stone were scalped, and stone of large size was dealt with; in some tests the fines were extracted from the feed and mixed with the product after crushing, and the final mix classified. To avoid disorganisation of the quarry procedure the batches of stone tested were the last skips tipped in any day's work.

The tests comprised: Obtaining the initial classification and weight of one or two skips of stone, passing the stone through the crusher, obtaining the classification again and comparing the final classification with the original classification, and comparing the particle form of the product of the different crushers. The crushers were not prepared for the tests and, taking the group as a whole, the general condition of the jaw faces was such as is usually found in average quarry practice; the procedure of feeding (apart from the tests when the feed was scalped) was also in agreement with normal quarry practice.

The different batches of stone dealt with in the various crushers were as follows:

(1) Crushers (a) and (b) operated on limestone obtained from the same quarry; both crushers were fed in the same way with batches of the same weight (5 tons) and stone of the same characteristics. One skip-load or the equivalent of each of the following classifications was dealt with in each machine: (1) A normal run-of-quarry stone from 34 in. to fines; (2) Hand-picked, "man-size," stone between 12 in. and 8½ in.; (3) Shovel-size stone, between 34 in. and 24 in.

(2) Crushers (c) and (d) operated on granite obtained from adjacent quarries having faces over 200 ft. deep and wherein the characteristics of the upper layer of stone differed but little from that of the lower layer. After initial blasting the large boulders were block-holed to obtain the size desired for feed. Two tests were carried out on each crusher dealing with mixed stone from the upper and lower face. The classification of the feeds was as follows:

*Jaw crusher* (c).—(1) Run-of-quarry, from 34 in. to fines; (2) Large stone, between 34 in. and 12 in.

*Gyratory crusher* (d).—(1) Run-of-quarry, from 24 in. to fines ; (2) Large stone, between 24 in. and 12 in.

(3) Crusher (e) was tested on limestone of two widely different characteristics obtained from the same quarry. These tests were on the same general lines as those already described ; the batches, however, were as follows :

Skips A, B, C, and F contained slabby stone having muddy seams ; skips D and E contained hard, clean, close-grained stone. Details are as follows :

Slabby, dirty stone.—Skip (A), run-of-quarry, from 24 in. to fines, choke feed ; skip (F), run-of-quarry, from 24 in. to fines, slow hand feed ; skip (B), hand feed, between 24 in. and 17 in. ; skip (C), hand feed, between 12 in. and 8½ in.

Clean hard stone.—Skip (D), hand picked, between 24 in. and 17 in. ; skip (E), hand picked, between 12 in. and 8½ in.

The product classification of skips A and F was of the same general nature and form ; the particle size of F, however, was rather larger. The reduction-ratio of the B and C batches was greater than that of D and E ; the particle size of the product was also rather larger though of the same general form.

For the purpose of analysis the feed and product of all stone was classified on sieves with square holes, the size of opening of each sieve having a ratio of $\sqrt{2}$, say 1·4 times that of the next sieve. Sieves were used with openings up to 6 in. ; above this dimension callipers were used and each piece of stone was measured in three directions to obtain a mean value.

The reports are very complete and include a large number of tables and graphs dealing with the stone experimented with. Some of the deductions drawn would, however, possibly need qualifying if the same batches and qualities of stone were dealt with in another machine of the same type or in other kinds of crusher.

The following general deductions can, however, be made.

(1) The size of stone (shovel size or man size) as fed to crushers (a) and (b) appears to have little bearing on the classification of the product ; the graph lines (in the report) of the two products almost coincide. The amount of fines in the man-size product, however, is rather greater than in the shovel-size product.

(2) The particle size and shape of product from the gyratory crusher and the single-roll crusher appear the same. There were cubes, slabs, and splinters in both products.

(3) The gyratory crusher produced the largest percentage of fines. This machine also produced less material larger than the crusher discharge opening than the other machine.

(4) The reduction-ratio appears to be greater in the gyratory crusher than in any other crusher tested.

(5) The greatest percentage of cubical product was reached at about the size of the discharge opening of each crusher. The product above and below this size tended to increase in flatness and slabbiness.

(6) The tendency to slabbiness appeared to vary with different classes of stone.

(7) The greatest percentage of any size stone is the size that approximates to the crusher opening ; this quantity was 5 per cent. greater in the gyratory crusher than in the jaw crusher.

(8) Shape or form of product appears to be a function of the reduction-ratio rather than of the type or the setting of the crusher. In a jaw crusher the smaller the reduction-ratio the more cubical will be the product.

(9) An increase in the reduction-ratio produces an increasing quantity of fines.

(10) Scalping the feed increases the production of aggregate-size stone with resultant reduction of fines.

(11) Choke feed produces more fines than controlled feed ; it also tends to produce a slabby shaped product rather than a cubical one.

(12) A regular feed avoiding surges tends to produce a more cubical form of product.

(13) Similar feed in crushers of any type with the same size discharge opening results in a similar reduction-ratio and the same general type and classification of product.

(14) There appears to be some indication that blasting and block-holing produce classification in mass generally similar to that produced by crushing.

These deductions are of a very general nature, and the original reports with graphs (which are issued by the United States Bureau of Mines, Washington) should be consulted for detailed information regarding any special features of crushing or crushing to a precise form and dimensions with avoidance of fines and waste.

## Recent Patents Relating to Cement and Lime.

### Coloured Cement.

491,051. P. Gerimont. August 24, 1937.

Portland cement or artificial hydraulic lime having a malachite green colour is produced by adding an oxide of chromium to the raw materials, sintering the mixture, cooling the clinker in a reducing atmosphere, and then reducing it to a powder.

### Cement, Lime, etc.

488,320. Metallges. Akt.-Ges. April 20, 1937.

Cement, lime, etc. are produced by sintering in blast-roasting apparatus, particularly of the suction type, spongy granules prepared by atomising raw meal through nozzles with a gaseous or vaporous medium such as air or the waste gases passing from the blast-roasting apparatus, impinging atomised water or steam on the atomised meal, and treating in a shaker conveyor or rotating drum to increase the size of the granules. The water, which may be atomised in the same nozzle as the meal, may contain foam-forming substances such as soap, tar, oils, and fatty oils. Alternatively the granules may be produced by blowing a hot gas or vapour, e.g. hot air, hot exhaust gases, or superheated steam in finely divided streams through a slurry of the raw material partially to dry it, the resulting granules being treated in a rotating drum before roasting. The slurry is placed in a vessel the bottom of which is provided with a large number of small holes or nozzles which may be covered by a protecting hood, and the treated contents may be tipped out or continuously discharged by scrapers ; or the slurry is treated from the outset in a rotary drum the shell of which is provided with nozzles through which the hot gases may be introduced.

# Relation of Compositions and Heats of Solution of Portland Cement Clinker.

By HERBERT INSLEY, EINAR P. FLINT, EDWIN S. NEWMAN, and J. ARTHUR SWENSON.

THE following is an abstract of a paper (Research Paper No. 1135) published by the United States National Bureau of Standards.

## Introduction.

It has long been recognised[1] that many of the properties of concrete are dependent in part on the relative proportions of the compounds present. Determinations of the contributions of individual compounds to the properties of cements and concretes[2, 3] have been based on the assumptions of previous investigators that cement clinker is completely crystalline and that no more than six phases—$3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, free CaO, and free MgO (periclase)—are present.

The accuracy of such methods depended in large part on the validity of these two assumptions. The recent development of a method for the microscopic examination of polished and etched specimens of Portland cement clinker using reflected light[4, 5] permits ready distinction of the constituents and precise determination of the boundaries of individual crystals. The combination of this method with one for measuring the relative amounts of the different constituents makes possible a quantitative and qualitative comparison of the phases actually present in the clinker with those calculated from the chemical analyses.

It is the purpose of the present paper to make such comparisons for a series of commercial cement-clinker samples and to compare the heats of solution obtained by calculation from microscopic measurement and chemical analysis with the experimentally determined heats of solution.

Twenty-six different samples of clinker were available from five different sources. These included ten samples of " modified low-heat " (type B) clinkers (designated by index letter T), three samples of clinker representative of " modified low-heat " cements (index letter W), and two samples of clinker representative of " low-heat " cements (index letter B). A fourth source was a group of 50 samples of clinker obtained through the U.S. Department of Agriculture (index letter M). Ten samples showing wide variations in composition were chosen from this group after a study of the analyses of the corresponding cements. A single sample obtained from the manufacturer (index letter P) is listed because its $Al_2O_3$ and $Fe_2O_3$ contents are low and its CaO content high.

The pure compounds used for the determination of heat of solution were obtained from several sources. Tricalcium aluminate and $4CaO.Al_2O_3.Fe_2O_3$, which were procured from Mr. William Lerch, were examined microscopically and found to be essentially homogeneous. Samples of CaO and MgO were obtained

by heating the chemically pure carbonates at about 1,400 deg. C., and $\beta 2CaO.SiO_2$ was made by heating $CaCO_3$ and $SiO_2$ in the proper proportions together with an amount of $H_3BO_3$ sufficient to give 0·2 per cent. of $B_2O_3$ in the final product.

**Preparation of Samples.**

The samples of commercial clinker weighed from 1 to 2 kg. About one-third of each sample was so crushed as to avoid the production of a large amount of fine material and then sieved. The material passing a No. 4 and retained on a No. 14 sieve was used for the experiments, one portion being reserved for chemical analysis, another for microscopic examination and a third for heat-of-solution measurements.

The usual methods of quantitative analysis were used for all determinations except those of the alkalis, in which case the J. Lawrence Smith method of decomposition was followed by the determination of $Na_2O$ by precipitation as sodium zinc uranyl acetate and of $K_2O$ as potassium chloroplatinate. Free CaO was determined by the ammonium-acetate method.[7]

**Microscopic Examination.**

For examination in polished etched preparations by reflected light the crushed clinker sample was placed in a shell vial of about 1·5 cm. inside diameter and immersed in Bakelite BR 0014 liquid resinoid. The preparation was evacuated in a vacuum desiccator by means of a faucet aspirator for two or three hours and then heated in an oven at about 80 deg. C. for about fifteen hours. The temperature was then raised to 100 deg. C. and the heating continued about seven hours or until the Bakelite was thoroughly hardened. After breaking the vial away, the lower surface of the preparation was ground down with No. 150 silicon carbide and water on a rotating lap until the clinker grains were exposed. Final grinding was done by hand with emery and alcohol on plate glass. The specimen was washed with alcohol and polished with rouge and alcohol on a canvas-covered disk rotating at about 1,200 revolutions per minute. The polished sections were examined with a vertical illuminator.[5]

A Wentworth recording micrometer[8] was used for quantitative microscopic analysis. This instrument has five micrometer screws, each one of which moves the specimen independently across the field beneath the reference cross hair in the eyepiece. The micrometer screw assigned to a particular constituent (phase) in the clinker is used for traversing grains of that constituent. The readings on the micrometer heads at the end of a complete traverse record the total linear intercepts for the different constituents. A series of traverses was made on each specimen, consecutive traverses being spaced at constant intervals. The specimens were of such a size that eleven traverses, 1 mm. apart, could be made. Assuming uniform distribution of constituents of sufficiently small grain size, the ratios of the linear intercepts of the constituents are equal to the volumetric ratios of the constituents in the specimen. The average of the micrometer readings on five different preparations was taken for the analysis of each sample brand. The average deviations from the mean were less than $\pm$ 2 per cent. for most samples.

| Clinker | Source [a] | Oxide composition | | | | | | | | | Free MgO (microscopic) | Free CaO | | $C_3S$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Loss on ignition | $SiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | CaO | $SO_3$ | $Na_2O$ | $K_2O$ | MgO | | Chemical | Microscopic | Calculated [b] | Microscopic |
| | | % | % | % | % | % | % | % | % | % | % | % | % | % | % |
| 1 | T | 0.26 | 22.02 | 4.90 | 4.20 | 63.86 | 0.23 | 0.07 | 0.27 | 4.31 | 2½ | 0.8 | ½ | 52.8 | 48 |
| 2 | T | .22 | 21.98 | 5.99 | 5.35 | 64.40 | .15 | .04 | .19 | 1.61 | <¼ | .1 | <¼ | 49.8 | 46 |
| 3 | B | .97 | 23.62 | 5.90 | 5.38 | 61.74 | .07 | .83 | .48 | 0.70 | <¼ | 0 | <¼ | 27.3 | 30 |
| 4 | W | .50 | 20.66 | 6.84 | 6.22 | 62.68 | .60 | .29 | .64 | 1.55 | <¼ | .5 | <¼ | 41.0 | 38 |
| 5 | B | .97 | 22.16 | 5.81 | 5.38 | 60.02 | .07 | .92 | .26 | 4.52 | 3 | .05 | <¼ | 39.0 | 37 |
| 6 | T | .83 | 22.16 | 5.21 | 4.77 | 63.18 | .25 | .17 | .31 | 3.08 | 1½ | .4 | <¼ | 46.7 | 54 |
| 7 | T | .36 | 21.03 | 5.01 | 5.08 | 63.14 | .47 | .12 | .48 | 4.39 | 2½ | 1.0 | 1 | 48.3 | 52 |
| 8 | T | 3.11 | 22.20 | 5.80 | 4.08 | 62.52 | .12 | .07 | .42 | 3.73 | 1½ | 1.6 | <¼ | 46.7 | 50 |
| 9 | T | 0.41 | 20.31 | 5.13 | 5.77 | 62.59 | .78 | .18 | 1.16 | 3.73 | 2½ | 0.5 | <¼ | 45.2 | 51 |
| 10 | T | .12 | 21.40 | 4.90 | 5.50 | 62.30 | .58 | .15 | 0.31 | 4.78 | 2½ | .1 | <¼ | 43.9 | 46 |
| 11 | T | .36 | 21.10 | 4.90 | 5.50 | 65.26 | .07 | .13 | .46 | 2.27 | ½ | .9 | ½ | 57.0 | 60 |
| 12 | T | .35 | 23.52 | 4.31 | 4.81 | 63.94 | .10 | .17 | .23 | 2.52 | 1½ | .5 | <¼ | 40.5 | 42 |
| 13 | T | 1.99 | 22.80 | 4.40 | 5.38 | 64.10 | .06 | .07 | .23 | 1.22 | <¼ | .8 | <¼ | 44.3 | 50 |
| 14 | W | 0.66 | 21.76 | 5.12 | 6.30 | 64.34 | .32 | .06 | .44 | 0.96 | <¼ | .8 | ½ | 42.2 | 47 |
| 15 | W | .47 | 22.26 | 5.05 | 6.33 | 63.24 | .73 | .11 | .66 | 1.24 | <¼ | .6 | 1 | 33.5 | 35 |
| 16 | M | .88 | 22.48 | 4.01 | 5.37 | 64.48 | .32 | .15 | .56 | 1.75 | <¼ | 0 | <¼ | 48.6 | 51 |
| 17 | P | .38 | 24.18 | 2.22 | 3.84 | 66.84 | .03 | .25 | .28 | 2.15 | <¼ | .1 | <¼ | 58.6 | 65 |
| 18 | M | .14 | 21.28 | 3.90 | 6.94 | 65.12 | .22 | .18 | .50 | 1.60 | ½ | .2 | <¼ | 47.3 | 51 |
| 19 | M | .87 | 19.62 | 3.50 | 7.24 | 66.62 | .59 | .20 | .60 | 0.84 | <¼ | .5 | ½ | 64.3 | 69 |
| 20 | M | .29 | 21.50 | 3.22 | 6.80 | 66.78 | .12 | .10 | .21 | 1.00 | <¼ | .5 | <¼ | 55.1 | 57 |
| 21 | M | .15 | 19.74 | 3.11 | 7.89 | 66.48 | .25 | .08 | .58 | 1.60 | <¼ | .8 | 1½ | 58.5 | 63 |
| 22 | M | .52 | 22.10 | 1.98 | 5.22 | 65.68 | .19 | .30 | .43 | 3.86 | 2 | .9 | 1 | 56.7 | 67 |
| 23 | M | .11 | 20.48 | 2.93 | 7.85 | 66.48 | .39 | .14 | .62 | 1.22 | 1 | .8 | 1 | 53.0 | 54 |
| 24 | M | .71 | 22.50 | 1.99 | 5.55 | 62.63 | .45 | .34 | 1.08 | 4.72 | 5 | .5 | <¼ | 37.9 | 47 |
| 25 | M | .48 | 21.08 | 2.21 | 6.39 | 66.92 | .04 | .13 | 0.14 | 2.61 | 1 | 1.6 | 2 | 58.5 | 71 |
| 26 | M | .27 | 23.10 | 1.97 | 7.35 | 65.44 | .08 | .19 | .39 | 1.29 | <¼ | 0.6 | <¼ | 35.2 | 41 |

[a] Index letters indicate source as follows: *T*=Tennessee Valley Authority type *B* clinker; *W*=Tygart River Valley modified "low heat" clinker; *M*=Miller's Series; *B*=Boulder Dam "low heat"; *P*=from producer.
[b] Compound composition calculated by the Bogue method from the chemical analysis.
[c] Heat of solution of glass—700 cal/g.
[d] Not determined.

All quantities excepting oxide composition ar

TABLE 2.—COMPOSITIONS AND HEATS OF SOL

| $C_3S$ | | $C_2S$ | | | Light interstitial | | | Total dark interstitial | | | Dark interstitial | | Glass (Lerch method) | Heat of solution [a] | | | $\frac{Al_2O_3}{Fe_2O_3}$ ratio |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Microscopic | Difference | Calculated [b] | Microscopic | Difference | Calculated $C_4AF$ [b] | Microscopic | Difference | Calculated $C_3A$ [b] | Microscopic | Difference | Crystalline [c] | Glass [c] | | Observed | Calculated from microscopic analysis [a] | Calculated from compound composition [b] | |
| % | | % | % | | % | % | | % | % | | % | % | % | *cal/g* | *cal/g* | *cal/g* | |
| 48 | −5 | 26.3 | 29 | 3 | 14.9 | 18 | 3 | 3.0 | 2 | −1 | ½ | 1½ | 3 | 632 | 621 | 629 | 0.86 |
| 46 | −4 | 25.6 | 27 | 1 | 18.2 | 25 | 7 | 4.1 | 2 | −2 | <¼ | 2 | 5 | 625 | 610 | 620 | .89 |
| 30 | 3 | 48.1 | 43 | −5 | 18.2 | 20 | 2 | 4.3 | 7 | 3 | 4 | 3 | (d) | 603 | 610 | 598 | .91 |
| 38 | −3 | 29.0 | 27 | −2 | 21.0 | 30 | 9 | 5.1 | 5 | 0 | ½ | 4½ | (d) | 616 | 625 | 613 | .91 |
| 37 | −2 | 32.9 | 33 | 0 | 18.0 | 23 | 5 | 4.3 | 4 | 0 | 1½ | 2½ | 5 | 615 | 618 | 618 | .92 |
| 54 | 7 | 28.9 | 23 | −6 | 15.9 | 19 | 3 | 4.1 | 2½ | −2 | ½ | 2 | 7 | 630 | 619 | 621 | .92 |
| 52 | 4 | 24.7 | 22 | −3 | 15.2 | 20 | 5 | 5.1 | 2½ | −3 | <¼ | 2½ | (d) | 634 | 624 | 634 | 1.01 |
| 50 | 3 | 30.4 | 27 | −3 | 11.9 | 18 | 6 | 4.7 | 3 | −2 | ½ | 2½ | (d) | 635 | 619 | 629 | 1.07 |
| 51 | 6 | 25.7 | 21 | −5 | 15.5 | 22 | 6 | 6.7 | 3½ | −3 | 1 | 2½ | 6 | 627 | 623 | 619 | 1.12 |
| 46 | 2 | 28.4 | 28 | 0 | 14.9 | 21 | 6 | 6.5 | 2½ | −4 | ½ | 2 | 3 | 628 | 618 | 626 | 1.12 |
| 60 | 3 | 17.7 | 11 | −7 | 14.9 | 23 | 8 | 6.5 | 5 | −2 | ½ | 4½ | 12 | 643 | 627 | 634 | 1.12 |
| 42 | 1 | 37.1 | 33 | −4 | 13.1 | 20 | 7 | 5.7 | 3 | −3 | <¼ | 3 | 10 | 624 | 613 | 615 | 1.12 |
| 50 | 6 | 32.3 | 29 | −3 | 13.6 | 18 | 4 | 7.2 | 3 | −4 | 1½ | 1½ | (d) | 619 | 616 | 617 | 1.22 |
| 47 | 5 | 31.1 | 24 | −7 | 15.6 | 24 | 8 | 8.3 | 4 | −4 | ½ | 3½ | (d) | 626 | 616 | 622 | 1.23 |
| 35 | 1 | 39.0 | 34 | −5 | 15.4 | 25 | 10 | 8.5 | 5 | −4 | 1 | 4 | 5 | 613 | 610 | 613 | 1.25 |
| 51 | 2 | 28.4 | 23 | −5 | 12.3 | 23 | 11 | 7.7 | 3 | −5 | ½ | 2½ | 11 | 629 | 620 | 623 | 1.34 |
| 65 | 8 | 25.4 | 18 | −7 | 6.8 | 12 | 5 | 6.4 | 5 | −1 | 3 | 2 | 8 | 638 | 628 | 633 | 1.73 |
| 51 | 4 | 23.3 | 17 | −8 | 11.8 | 22 | 10 | 12.4 | 9 | −3 | 5 | 4 | 5 | 632 | 629 | 632 | 1.78 |
| 69 | 5 | 8.2 | 3 | −5 | 10.7 | 10 | −1 | 13.6 | 17 | 3 | 8 | 9 | 13 | 647 | 651 | 629 | 2.07 |
| 57 | 2 | 20.3 | 17 | −3 | 9.8 | 11 | 1 | 12.8 | 15 | 2 | 12 | 3 | (d) | 638 | 643 | 642 | 2.11 |
| 63 | 5 | 12.7 | 7 | −6 | 9.5 | 7 | −3 | 15.9 | 21 | 5 | 11 | 10 | (d) | 646 | 658 | 651 | 2.53 |
| 67 | 10 | 20.8 | 11 | −10 | 6.0 | 6 | 0 | 10.7 | 13 | 2 | 6 | 7 | (d) | 652 | 649 | 644 | 2.64 |
| 54 | 1 | 18.7 | 14 | −5 | 8.9 | 10 | 1 | 16.0 | 20 | 4 | 14 | 6 | (d) | 639 | 656 | 644 | 2.68 |
| 47 | 9 | 36.1 | 26 | −10 | 6.1 | 7 | 1 | 12.4 | 15 | 3 | 6 | 9 | (d) | 641 | 646 | 630 | 2.78 |
| 71 | 12 | 16.7 | 3 | −14 | 6.8 | 5 | −2 | 13.4 | 18 | 5 | 8 | 10 | 13 | 660 | 661 | 654 | 2.89 |
| 41 | 6 | 39.8 | 35 | −5 | 6.0 | 6 | 0 | 16.4 | 18 | 2 | 14 | 4 | (d) | 631 | 637 | 619 | 3.73 |

[a] Heats of solution used in calculations:

| Compound | cal/g |
|---|---|
| $C_3A$ | 799 |
| $C_3S$ | 639 |
| $C_2S$ | 572 |
| $C_4AF$ | 592 |
| MgO | 876 |
| CaO | 848 |

[c] Microscopically determined.

position are calculated on an ignition-loss-free basis.

TS OF SOLUTION OF COMMERCIAL CLINKER SAMPLES.

In recalculating volume percentages to weight percentages, the density values were as follows: $\beta 2CaO.SiO_2$, 3·28[9]; $3CaO.SiO_2$, 3·13[10]; $4CaO.Al_2O_3.Fe_2O_3$, 3·77.[10] Because the composition of the glass phase is variable and indeterminable, a value of 3·00 for the density of $3CaO.Al_2O_3$, found by averaging two previously determined values[10, 11], was used for the total "dark interstitial" material.

The preparations were first etched with water for two seconds, immediately rinsed with alcohol, and dried. This etching served to distinguish free MgO, free CaO, and crystalline "dark interstitial" material[12] from the rest of the clinker constituents. After quantitative microscopic analysis for these three constituents, the preparation was etched for three seconds in a 1 per cent. alcoholic solution of $HNO_3$ to differentiate $2CaO.SiO_2$, $3CaO.SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and total "dark interstitial" material. Thin sections and polished thin sections[12] were also made of a few samples.

## Heat of Solution.

The heats of solution of the clinker samples and of the pure compounds were determined at 25 deg. C. with an isothermal calorimeter[13,14] in a solvent consisting of a mixture of 648·5 g. of 2. 500 $\pm$ 0·002 *N* $HNO_3$ and 11·5 g. of reagent quality HF (48 per cent.). All experimental heats of solution were calculated on an ignition-loss-free basis. The values of the heats of solution of the pure compounds used in the computation of the heats of solution of the clinkers as derived from chemical and microscopic analysis are given in *Table* 1. Differences between these values and those given by Lerch and Brownmiller[15] for the same compounds may be attributed to differences in calorimeters and to volumes and concentrations of the solvents used. In calculating the heat of solution of glass, a value of 700 cal. per gr. was used. This value represents an approximate mean of the values reported by Lerch and Brownmiller for glasses with the same range in $Al_2O_3/Fe_2O_3$ ratios as the clinker samples in the present paper.

TABLE 1.—HEATS OF SOLUTION OF PURE COMPOUNDS.

| Compound. | Heat of solution. | Ignition loss. |
|---|---|---|
| | cal/g | Per cent. |
| $3CaO.SiO_2$ .. .. .. | 639 | 0·51 |
| $\beta 2CaO.SiO_2$ .. .. | 572 | ·71 |
| $4CaO.Al_2O_3.Fe_2O_3$ .. .. | 592 | ·14 |
| $3CaO.Al_2O_3$ .. .. .. | 799 | ·17 |
| MgO .. .. .. | 876 | (*a*) |
| CaO .. .. .. | 848 | (*a*) |

(a) MgO and CaO were freshly ignited.

## Quantitative Determinations.

The results of chemical analysis, quantitative microscopic analysis, and heat-of-solution determinations are given in *Table* 2. The designations $C_3S$ ($3CaO.SiO_2$) and $C_2S$ ($2CaO.SiO_2$) are used for both calculated compound composition and microscopic analysis. The constituent designated "light interstitial" by microscopic analysis is considered equivalent to $C_4AF$ ($4CaO.Al_2O_3.Fe_2O_3$)

by calculation, and the constituent designated " total dark interstitial " by microscopic analysis is considered the nearest equivalent to $C_3A$ ($3CaO.Al_2O_3$) by calculation. The values given in the column headed " crystalline dark interstitial " are for material rapidly etched by $H_2O$ and determined microscopically. The difference between that value and the value found under the heading, " total dark interstitial," is recorded in the column under " dark interstitial—glass." Determinations of glass by the heat-of-solution method[15] are recorded in the column designated " Glass—Lerch Method."

**Qualitative Microscopic Examination.**

(a) $3CaO.SiO_2$.—The samples show a wide range in size and perfection of outer form of the tricalcium silicate crystals. The crystals of this compound are on the average larger than those of any other compound, but the variation in size is large, not only from one lot of clinker to another, but from one piece of clinker to another. The crystals in some samples show considerable perfection of form, the individuals in polished section having straight edges and sharp angles. In other samples there is marked corrosion with rounding of angles and deep embayment of edges. The tricalcium silicate crystals in samples with low $Al_2O_3/Fe_2O_3$ ratios have greater perfection of form, whereas the crystals in samples with high $Al_2O_3/Fe_2O_3$ ratios are deeply corroded and embayed. The corroded crystals are generally, although not always, surrounded by a fringe of minute crystals of $2CaO.SiO_2$.

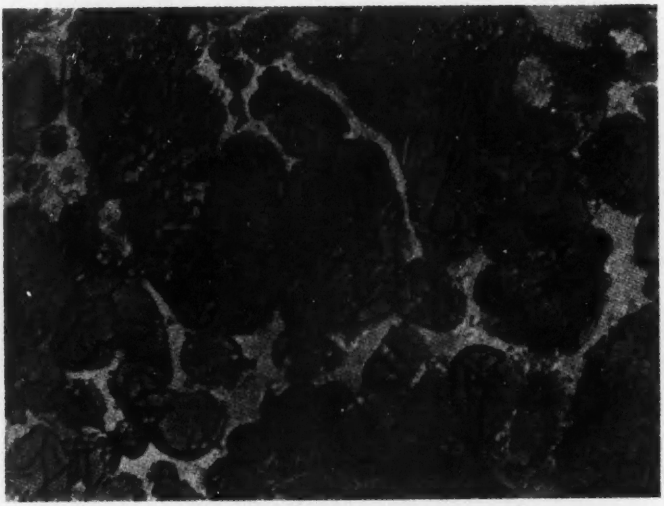
The existence of zoning in $3CaO.SiO_2$, and its relation to solid solution, have been noted.[5] Some degree of zoning is present in all the samples studied, although in several cases it can be observed only under the most favourable etching conditions. The most satisfactory etching conditions to produce evidence of zoning were three seconds at 25 deg. C. in a solution of 1 per cent. of $HNO_3$ in alcohol. The most pronounced zoning was observed in tricalcium silicate crystals in samples 10, 23, and 26, whereas samples 6, 8, 11, 12, and 16 exhibited very little zoning. The zone boundaries generally parallel the crystal edges, although infrequently the boundaries appear to be curved or irregular. Rhythmic zoning is not unusual, weakly etched alternating with strongly etched zones. The degree of etching and the development of the zoning are affected considerably by the orientation of the crystals. Surfaces parallel to basal faces etch weakly and show no zoning, whereas surfaces normal to basal faces etch most strongly and show the greatest development of zoning. No close relation between the zoning of $3CaO.SiO_2$ and the composition of the clinker has been found.

Solid solution in $3CaO.SiO_2$ crystals is shown by other optical evidence as well as zoning. Samples which contain crystals that show strong zonal etching also contain crystals with marked zonal extinction when examined petrographically. A change in index of refraction from interior to exterior of such crystals or from a strongly zoned to an unzoned crystal is, however, not detectable.

(b) $2CaO.SiO_2$.—All dicalcium silicate in industrial clinker is believed to be of the beta form. Three types of $\beta 2CaO.SiO_2$ differing somewhat in twinning

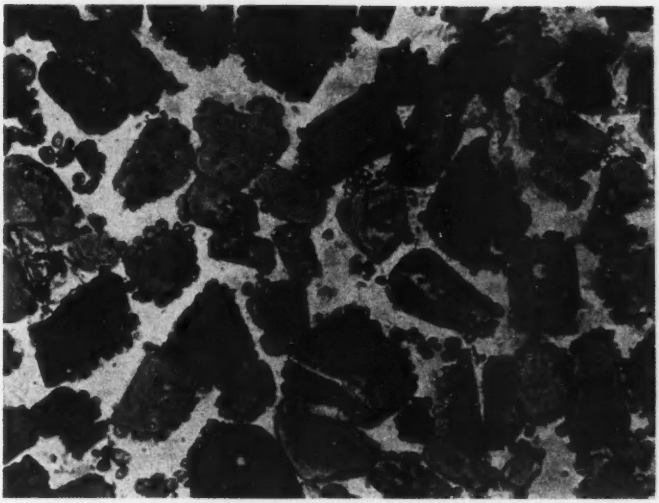
Etched with 4 per cent. alcoholic solution of $HNO_3$. Reflected light. Magnification × 1000.

**Fig. 1.—$2CaO.SiO_2$ of Types Ia and III in Clinker Sample No. 17.**



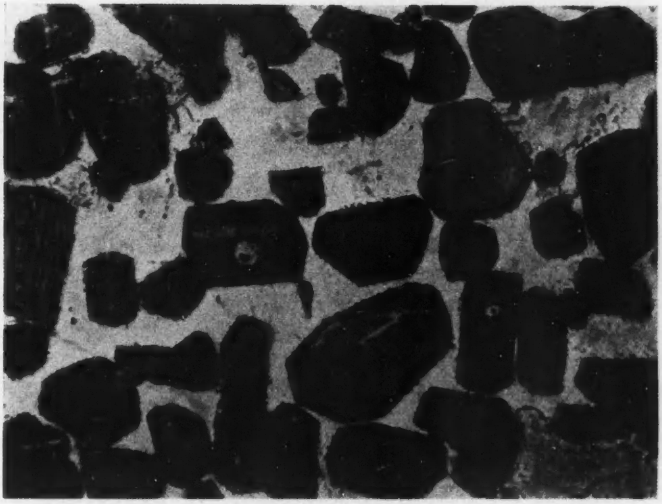
Etched with 1 per cent. alcoholic solution of $HNO_3$. Reflected light. Magnification × 500.

**Fig. 2.—$2CaO.SiO_2$ of Types Ia and III in Clinker Sample No. 26.**



From Clinker Sample No. 21. Etched with 1 per cent. alcoholic solution of $HNO_3$. Reflected light. Magnification ×500.

**Fig. 3.—Corroded Crystals of $3CaO.SiO_2$ Fringed with unusually large rounded grains of $2CaO.SiO_2$.**



From Clinker Sample No. 21. Etched with 1 per cent. alcoholic solution of $HNO_3$. Reflected light. Magnification ×500.

**Fig. 4.—Corroded Crystals of $3CaO.SiO_2$ Fringed with rounded grains of $2CaO.SiO_2$ of Normal Size.**

and in habit have been distinguished. These were named types I, II, and III in a previous paper.[5] Another variant has been observed in many clinker specimens in the present investigation. It is called type Ia and is distinguished from type I by the presence of discrete particles along what are apparently traces of twinning planes (*Figs.* 1 and 2). This structure is believed to be caused, according to Tavasci's theory,[4] by unmixing during cooling of a material in solid solution in $2CaO.SiO_2$.

Examples of all four types have been found in the specimens studied. Type II, containing a single set of parallel twinning lamellæ, occurs only in samples 4 and 15. Type III, often containing irregular cracks or veinlets but without distinctive twinning lamellæ, occurs sometimes as overgrowths on crystals of types I and Ia and sometimes as individual crystals. Types I and Ia are sometimes found in the same clinker piece. Crystals of type I are more abundant than those of any other type in the majority of the samples. All of the dicalcium silicate crystals studied exhibit rounded or serrated edges with no evidence of regular external form.

In many of the specimens crystals of $3CaO.SiO_2$ are surrounded by a fringe of minute rounded particles (*Figs.* 3 and 4). Although these particles are generally too small to show the characteristic internal structure with the microscope, their etching behaviour indicates that they are $2CaO.SiO_2$. This fringing material generally surrounds $3CaO.SiO_2$ crystals exhibiting considerable corrosion and embayment and, therefore, it has been found in samples with the higher $Al_2O_3/Fe_2O_3$ ratios. The other types of $2CaO.SiO_2$ apparently bear no relation to the chemical composition of the clinker samples.

Crystals of dicalcium silicate show a wide range in size, but are in general smaller than those of the tricalcium silicate.

(c) "LIGHT INTERSTITIAL" MATERIAL.—In the investigation of clinker by the reflecting microscope, two types of interstitial material have been differentiated which have been called "light interstitial" material and "dark interstitial" material[12]. The evidence indicates that the light interstitial material is crystalline with optical properties like those of $4CaO.Al_2O_3.Fe_2O_3$. The light interstitial material is intimately associated with the dark interstitial in most of the clinker specimens. Not only the size of the aggregates but the size of the individual crystals appear to bear some relation to the chemical composition, those clinker samples with the lower $Al_2O_3/Fe_2O_3$ ratios generally containing the larger crystals of $4CaO.Al_2O_3.Fe_2O_3$. The form of the crystals is also somewhat dependent on chemical composition. When the $Al_2O_3/Fe_2O_3$ is low the crystals of $4CaO.Al_2O_3.Fe_2O_3$ have good prismatic development with straight edges, but when the $Al_2O_3/Fe_2O_3$ ratio is high the faces are poorly developed, probably because they form at a later stage of the crystallisation of the clinker.

Most of the $4CaO.Al_2O_3.Fe_2O_3$ crystals found in commercial cement clinker are pleochroic, but the pleochroism varies widely from one clinker sample to another and even from one crystal to another in the same sample. This variation appears to have no relation to the chemical composition of the sample. In one sample examined (No. 4) the larger crystals were light amber in colour with no

perceptible pleochroism, whereas the smaller crystals in the same clinker piece were much darker and exhibited strong pleochroism.

(d) "DARK INTERSTITIAL" MATERIAL.—The dark interstitial material has been classified into crystalline and glassy types. One method of distinction is the rate of reaction with water when used as an etching reagent, the former type being rapidly etched and the latter slowly etched. The crystalline dark interstitial material can be subdivided into a rectangular isotropic form and a prismatic anisotropic form, whereas the glassy type has a variable index of refraction and is apparently isotropic when observed in thin section or powdered form.

In the samples investigated the rectangular crystalline form, which has the optical properties of $3CaO.Al_2O_3$, is found in only two samples (20 and 21) and there in only very small amounts. The anisotropic prismatic form, which appears to be produced only in the presence of alkali,[12] is a much more abundant constituent. It occurs to some extent in all the samples examined; in samples with low $Al_2O_3/Fe_2O_3$ ratios it is present in small amounts and in localised clusters of crystals as if it were the result of non-uniformity of the mix, whereas in other samples the prismatic crystals are distributed more uniformly.

The dark interstitial material which reacts slowly with water has been found to some extent in all the samples. Although it is impossible to measure the indices of refraction of this phase accurately, those samples having low $Al_2O_3/Fe_2O_3$ ratios contain glass which is microscopically colourless with an index of refraction less than 1·72, whereas those with high $Al_2O_3/Fe_2O_3$ ratios contain glass with an index higher than 1·72 and with a green colour. In all the samples the glassy phase is intimately mixed with the prismatic crystals of $4CaO.Al_2O_3.Fe_2O_3$.

(e) FREE MgO.—Free MgO occurs as angular grains with the optical properties of periclase. These have been identified in polished sections of commercial clinker.[12] In the present investigation free MgO has been seen in the majority of the samples. Although the magnesia grains are small, in general, the greater the amount of MgO the larger the grain size of the periclase. The free MgO is associated with the interstitial material in all the samples. In most of the samples the periclase grains are more or less uniformly distributed throughout the specimens examined, but in some (notably No. 5) the grains occur in clusters. This may be the result of improper mixing of raw materials.

(f) FREE CaO.—Free CaO occurs as rounded grains which are detected by etching reactions previously described.[12] In most of the samples the free CaO grains are present as clusters associated with concentrations of $3CaO.SiO_2$ crystals and therefore are probably the result of some lack of uniformity in the batch.

## Discussion.

A comparison of direct and indirect methods of quantitative determination of the phases present in Portland cement clinker shows certain systematic relations (*Table* 2). These are most apparent when the columns headed "difference" are examined. These columns show the differences between the values for equivalent constituents as determined microscopically and chemically. The

percentages of $2CaO.SiO_2$ determined microscopically exceed those determined chemically only for two samples with the lowest $Al_2O_3/Fe_2O_3$ ratios, whereas the percentages of $3CaO.SiO_2$ obtained microscopically are less than those obtained chemically only for samples with low $Al_2O_3/Fe_2O_3$ ratios. The microscopic values for " light interstitial " material tend to be greater than those for calculated $4CaO.Al_2O_3.Fe_2O_3$ for samples with low $Al_2O_3/Fe_2O_3$ ratios, but the differences are close to zero for samples with $Al_2O_3/Fe_2O_3$ ratios of 2·00 or greater. The reverse is true when microscopically determined total " dark interstitial " material is compared with calculated $3CaO.Al_2O_3$. The microscopic values are less than or equal to the calculated (with one exception) for low $Al_2O_3/Fe_2O_3$ ratios and greater than the calculated for ratios more than 2·00.

Several reasons may be given for the differences between the compositions determined microscopically and those obtained by calculation. The fact that tricalcium silicate contains other material in solid solution would tend to make the observed amount greater than that obtained by calculation by the Bogue method[16] as pure $3CaO.SiO_2$. Moreover, Lea and Parker[19] have shown from a consideration of the system $CaO\text{-}Al_2O_3\text{-}Fe_2O_3\text{-}SiO_2$ that cement clinkers with high $Al_2O_3/Fe_2O_3$ ratios contain greater amounts of $3CaO.SiO_2$ and lesser amounts of $2CaO.SiO_2$ when crystallisation is arrested during cooling than when complete equilibrium is attained.

Because there is partial solid solution between $4CaO.Al_2O_3.Fe_2O_3$ and $3CaO.Al_2O_3$ in the system $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$,[20] it seems probable that the excess of observed light interstitial material over calculated $4CaO.Al_2O_3.Fe_2O_3$ in clinker with low $Al_2O_3/Fe_2O_3$ ratios may be explained by the earlier crystallisation of $4CaO.Al_2O_3.Fe_2O_3$ with solid solution of material approximating $3CaO.Al_2O_3$ in composition. In clinkers with high $Al_2O_3/Fe_2O_3$ ratios, dark interstitial material may be expected to crystallise first and to take some $4CaO.Al_2O_3.Fe_2O_3$ into solid solution. The prismatic doubly-refracting constituents[12] presumably produced by alkalis are not accounted for in the Bogue method of calculation. Their presence would tend to increase the amount of dark interstitial material, but what the quantitative effect would be on the discrepancies between calculated and microscopically determined compositions is not known.

To account for the rather large differences between the light interstitial constituent and calculated $4CaO.Al_2O_3.Fe_2O_3$ in some samples, it has been suggested that the light interstitial constituent may consist of another phase besides $4CaO.Al_2O_3.Fe_2O_3$, for instance, a highly-refractive iron-bearing glass which is not distinguished from $4CaO.Al_2O_3.Fe_2O_3$ by the etching reagents used. Attempts to differentiate the light interstitial material into two phases by the use of other etching reagents and illuminating methods have thus far been unsuccessful.

In the Bogue method all the MgO is calculated as free MgO (periclase). In all but one of the samples examined the free MgO as determined by microscopic analysis is less than the total MgO by chemical analysis. Evidently a part of the MgO is dissolved in the glass or in one or more of the crystalline constituents.

The agreement between the microscopic method and the ammonium acetate method in the determination of free CaO is, in general, good. The somewhat lower results by the microscopic method for most samples are to be expected because the chemical method includes both free $Ca(OH)_2$ and free CaO, whereas the microscopic method distinguishes only crystalline CaO. The large difference for sample 8 is probably to be attributed to a partial hydrolysis of the clinker constituents, as indicated by the high ignition loss.

Although the presence of glass is evidence that commercial clinkers are not the product of crystallisation under equilibrium conditions, the simultaneous occurrence of fine-grained crystalline light and dark interstitial material with glass in the same specimen indicates also that the clinkers have not been completely quenched. The commercial product may, therefore, be considered as an intermediate stage between a material quenched from a definite temperature and one crystallised at continuous equilibrium conditions.

In comparing calculated and observed heats of solution (*Table* 2) it is evident that, in general, the heats of solution as computed from calculated compound composition agree somewhat better with the observed than do those calculated from microscopic analysis, the average difference between observed and microscopic analysis being 8·3 cal. per gr. and between observed and calculated compound composition being 5·6 cal. per gr. In making the heat of solution calculations based upon the Bogue method of determining compound composition it was assumed that: (1) The compounds calculated to be present had the compositions and the heats of solution of the pure compounds unaffected by solid solution; (2) The oxides present in minor amounts, such as alkalis, did not enter into compounds or affect the heats of solutions; and (3) Perfect equilibrium crystallisation took place during cooling without the formation of glass.

In making the calculation of heats of solution from microscopic analyses it was not only necessary to use the heats of solution of the pure compounds but also to use the heat of solution of $3CaO.Al_2O_3$ for all the crystalline dark interstitial material, whether rectangular or prismatic. A constant value of 700 cal. per gr. was used for all the glass, although the composition and consequently the heat of solution of the glass vary with the composition and rate of cooling of the clinker specimen.

All the assumptions made with respect to both types of calculation are known to be inexact, but they are felt to be the closest approximations that can be made at the present state of knowledge. Considering the errors in the basic assumptions, the degree of correspondence of either of the methods of calculation with the observed heats of solution has little significance.

The glass content by the Lerch method (*Table* 2) is greater than the glass content by the microscopic method for all samples on which determinations were made. Because the Lerch method is essentially a heat-of-solution method it is open to some of the same errors (already pointed out by Lerch and Brownmiller[15]) that affect the calculation of heat of solution from compound compositions, namely, the assumption that the compounds present are free from

solid solution and the assumption that the alkalis and other minor oxides have no effect on the heat of solution. The accuracy of the method will be increased as more knowledge is obtained on the actual composition and properties of these compounds in cement clinker.

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## Memorial to Joseph Aspdin.

At St. John's Church, Wakefield, on November 24, Lord Wolmer, on behalf of the cement industry, presented a pair of iron gates and a bronze tablet to the parish of St. John's, Wakefield, in memory of Joseph Aspdin, the inventor of Portland Cement. A memorial service was conducted by the Vicar of Wakefield. Among the guests present were the Lord Bishop of Wakefield, the Mayor of Wakefield and descendants of Joseph Aspdin.

# The Permeability of Cement Mortar.

A NEW relation between permeability and solubility has been reported to the Association of Japanese Portland Cement Engineers by Mr. K. Tominaga, in a paper in which the writer described his experimental results on permeability.

Ordinary commercial cement (A) and mixed commercial cement (B) were used with natural silica sand (particle dimension = 2·50 mm.) in making the test specimens. The ratios of cement to sand used were 1 : 3, 1 : 5 and 1 : 7, and the water-cement-ratio was such as to give a constant consistency. The tests were made at the age of 28 days under a hydraulic pressure of 0·5–6·0 kg./cm². The specimens were cured in water and the temperatures of testing were 22 deg. C. (mean), min. 20 deg. C. and max. 25 deg. C. The outside diameter of the specimen was 150 mm., the inside diameter 100 mm., and the height 100 mm. Tests were made of the permeability in c.c. per hour and the solubility ($Ca(OH)_2$ in 100 c.c. of permeated water).

### Relation between Permeability and other Conditions.

The greater the cement-sand-ratio the smaller the permeability was found (*Fig.* 1), and as the material aged its permeability became less (*Fig.* 2). The tests showed that as the hydraulic pressure was increased the permeability also became greater (*Fig.* 3). Typical examples of the reduction of permeability with lapse of time under pressure are shown in *Fig.* 4.

### Relation between Solubility of Calcium Hydroxide Dissolved in Permeating Water and other Factors.

When water passes through mortar a large quantity of the hardening element is extracted with it (see *Table* 1). This consumption of the hardening element has an important effect on the durability of the cement. The chief component of the solute being calcium hydroxide, this was investigated and the following conditions were found to have a great effect on the solubility of calcium hydroxide.

(1) Solubility decreases as the cement-sand-ratio becomes larger (*Table* 2).
(2) As the material ages the solubility decreases (*Fig.* 5).
(3) As the hydraulic pressure increases the solubility becomes large (*Fig.* 6).
(4) Solubility decreases with lapse of the time under pressure.

TABLE 1.—SOLUTES (GRAMMES IN 100 C.C.) IN PERMEATED WATER.

| Age. | "A" Cement. | | | | "B" Cement. | | | |
|---|---|---|---|---|---|---|---|---|
| | Pressure. | $SiO_2$. | $R_2O_3$. | CaO. | Pressure. | $SiO_2$. | $R_2O_3$. | CaO. |
| 7 | 0·5–2·5 | 0·0034 | 0·0026 | 0·1005 | 1·0–3·0 | 0·0006 | 0·0004 | 0·0807 |
| 14 | 2·5–3·5 | 0·0012 | 0·0009 | 0·0471 | 2·0–4·0 | 0·0011 | 0·0011 | 0·0441 |
| 28 | 4·5–5·5 | 0·0011 | 0·0021 | 0·0435 | 4·5–5·5 | 0·0015 | 0·0007 | 0·0141 |

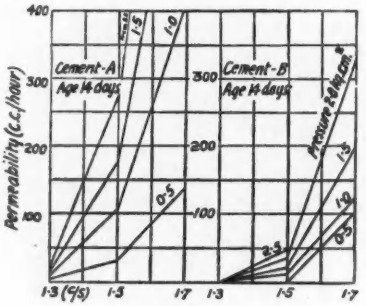


Fig. 1.

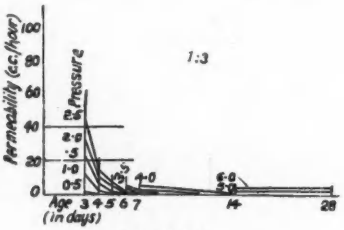


Fig. 2 (a).

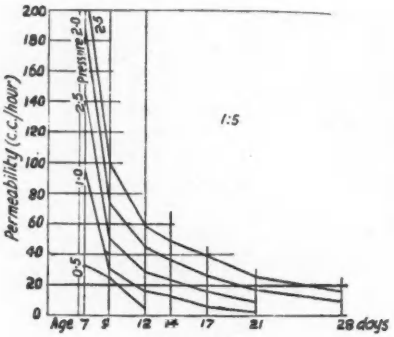


Fig. 2 (b).

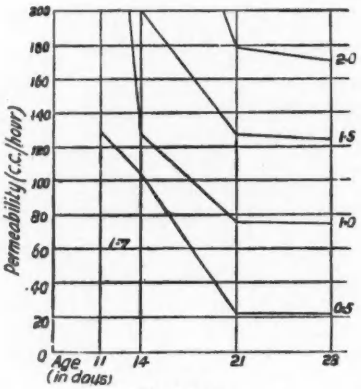


Fig. 2 (c).

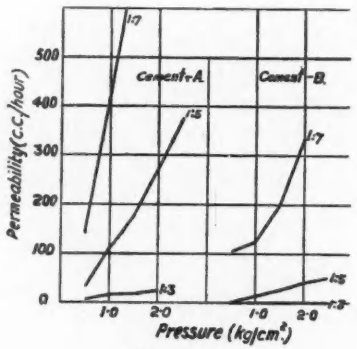


Fig. 3 (a).

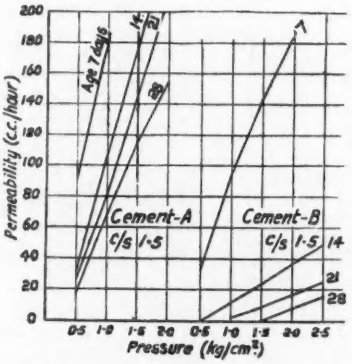


Fig. 3 (b).

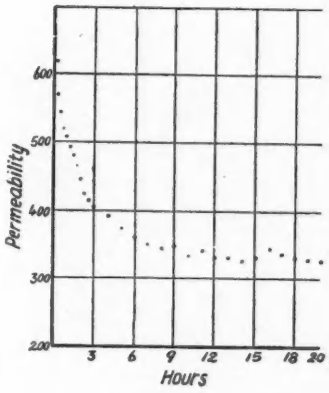


Fig. 4 (a).—Typical Reduction of Permeability with Age.

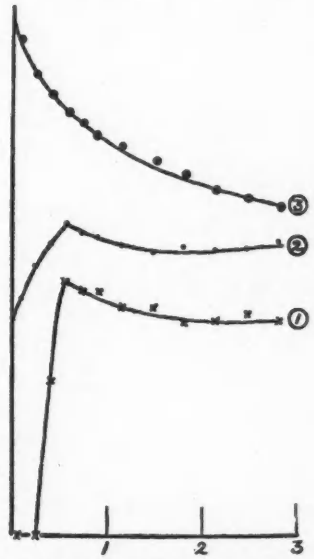


Fig. 4 (b).—Three Typical Reductions of Permeability (in early period).

TABLE 2.—$Ca(OH)_2$ (GRAMMES IN 100 C.C. OF WATER).

| Cement. | Ratio of Cement to Sand. | | |
|---|---|---|---|
| | 1 : 3. | 1 : 5. | 1 : 7. |
| A | 0·0347 | 0·1198 | 0·1623 |
| B | 0·0066 | 0·0400 | 0·0990 |

**Relation between Solubility and Quantity of Permeating Water.**

As mentioned previously the quantity of permeated water and its solubility are affected by the same factor, so there must be a functional relation among

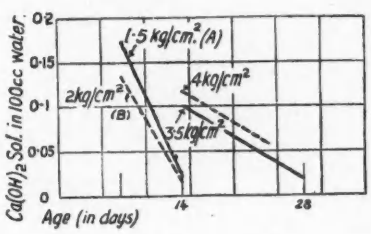


Fig. 5.

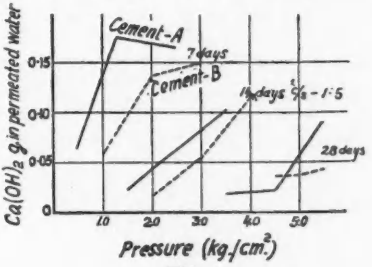


Fig. 6.

these. Now, if we neglect classification of cement, ages, the cement-sand-ratio, hydraulic pressure, and other conditions, the following relations are found (*Fig.* 7) :

(1) To some extent solubility of calcium hydroxide is proportional to the quantity of permeated water.

(2) After the solubility reaches 0·17 g. per 100 c.c., or comes to the saturation point of calcium hydroxide, the solubility becomes constant irrespective of the quantity of permeated water. (The solubility of calcium hydroxide in saturated solution is roughly equal to 0·17 g. per 100 c.c.)

This shows the relation between the permeability and the amount of dissolved substance.

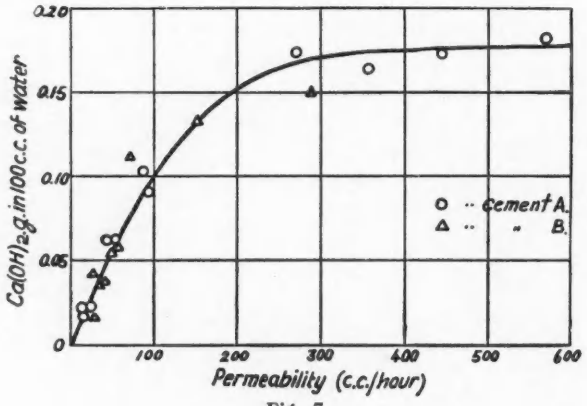


Fig. 7.

The weight of dissolved calcium hydroxide = C × solubility × permeability, in which C is a constant. But solubility = K × permeability, therefore the weight of dissolved calcium hydroxide = K × (permeability)$^2$. That is, the weight of calcium hydroxide dissolved in permeated water is proportional to the square of the permeability, which is a very important factor in the durability of cement.

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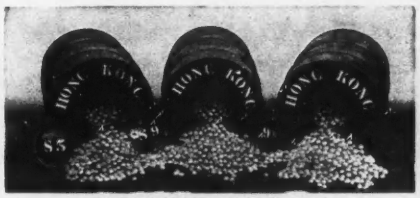


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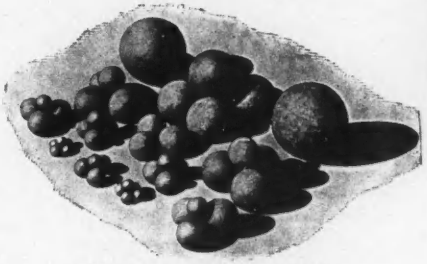

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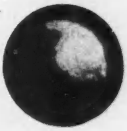

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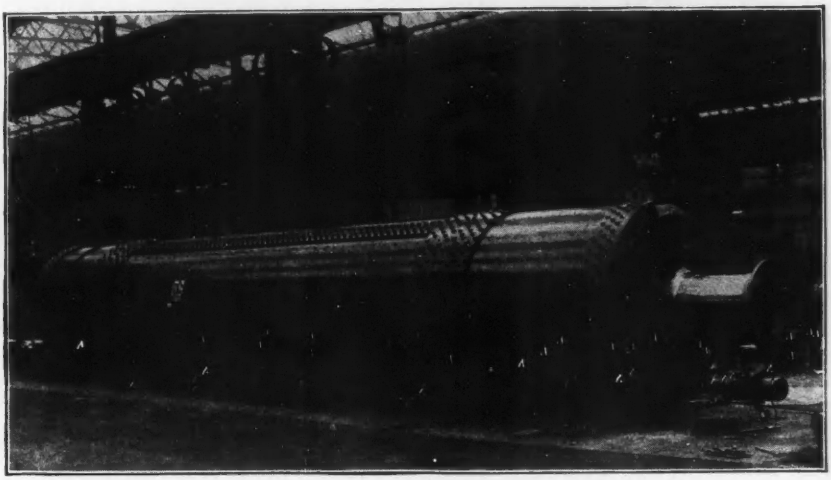

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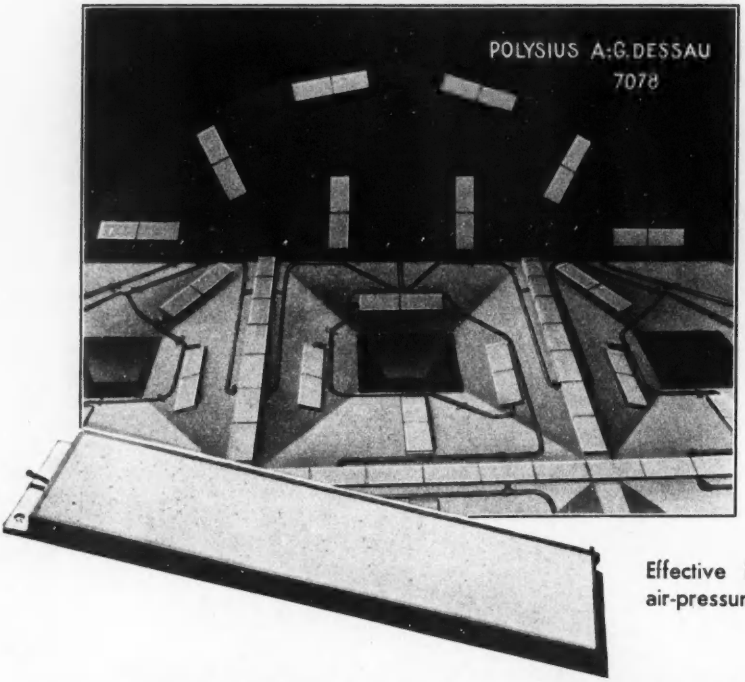


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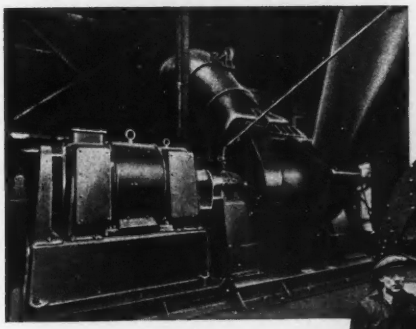

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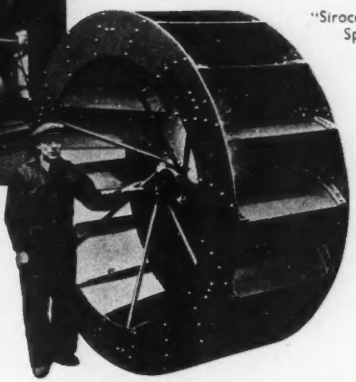

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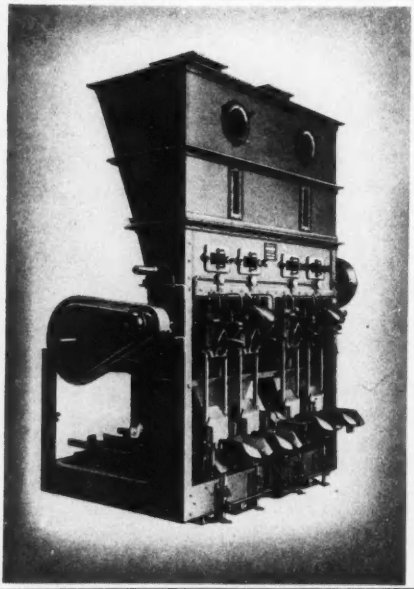

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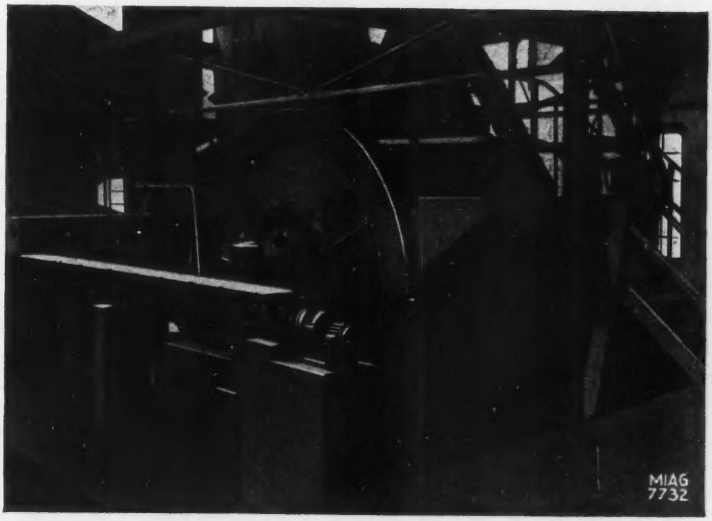


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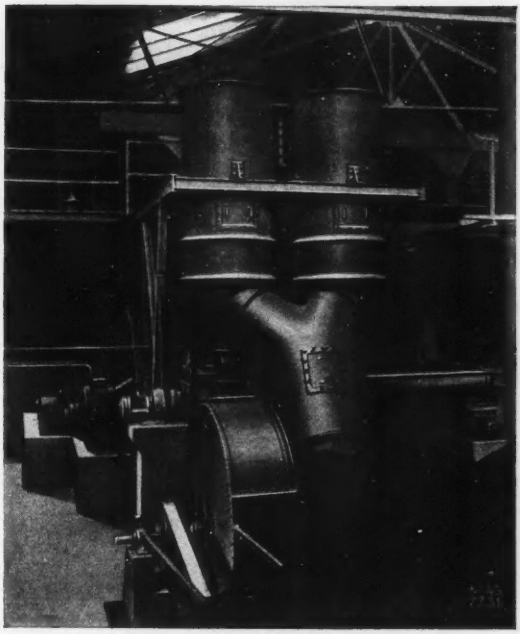

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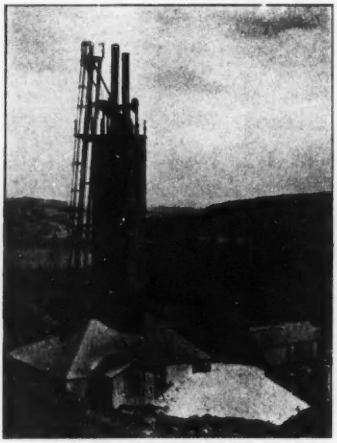

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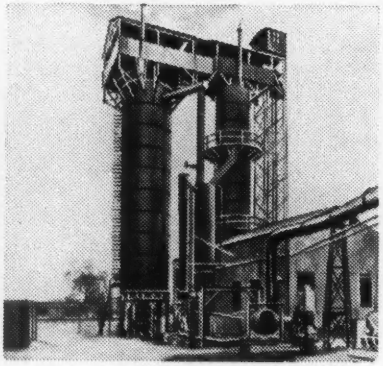

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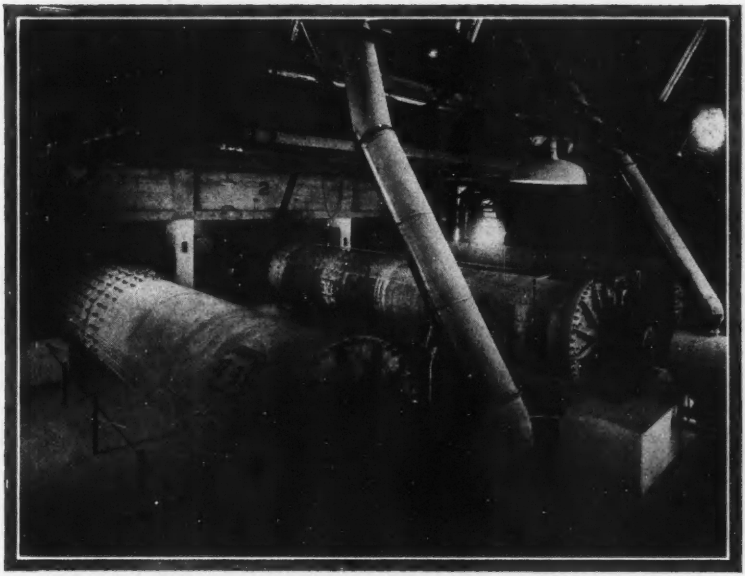

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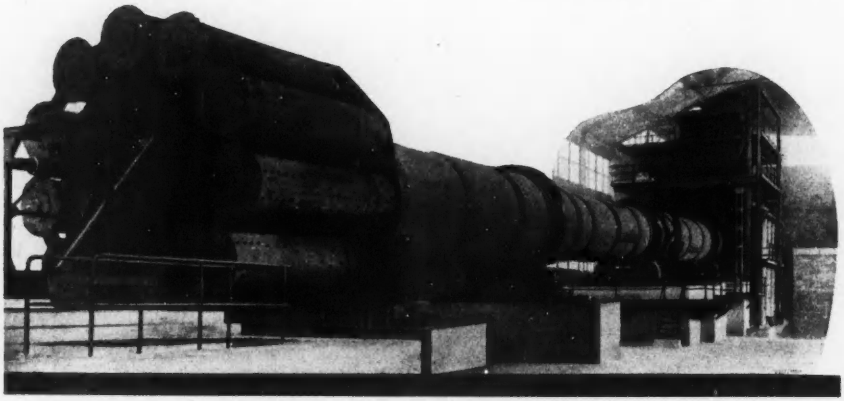

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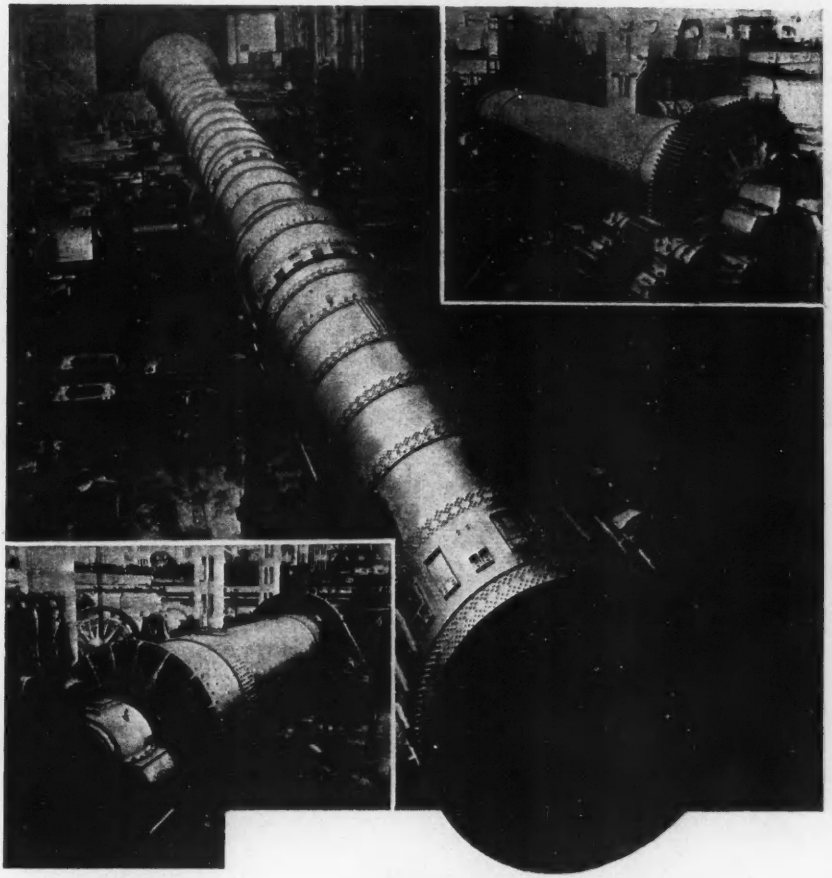

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Published by CONCRETE PUBLICATIONS, LTD., 14, Dartmouth Street, London, S.W.1, England.
Printed in Great Britain by THE CORNWALL PRESS LTD., 1-6, Paris Garden, Stamford Street, London, S.E.1.